AEROCOLLOID FORMATION FROM MATERIAL UNDER IRRADIATION

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Eddie B. Bock

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AEROCOLLOID FORMATION FROM MATERIAL UNDER IRRADIATION

Approved:

Clyde Orr, Jr., Chairman

John B. Muzzy

Henderson C. Ward

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NOMENCLATURE

A	Electrode area (cm^2)
Hz	Measurement of frequency (cycles/second)
ΔF	Change in resonance frequency (Hz)
F_o	Resonant frequency of crystal (MHz)
μg	Microgram
ΔM	Particulate mass added to the electrode surface of the crystal (μg)
Δt	Sampling time (seconds)
Q	Sampled aerosol flow rate ($meters^3$/second)
S	Theoretical mass sensitivity (Hz/μg)
E_c	Efficiency of particle collection by the collector
E_w	Efficiency of the piezoelectric particle microbalance in weighing the deposited particles
M	Mass of particles collected (μg)
I	Light intensity (watts/cm^2)

SUMMARY

The presence of aerocolloids is associated with poor visibility and a lowering of sunlight intensity caused by the scattering of light from the particles. In the past, the formation of aerocolloids was thought to be produced exclusively from photochemical reactions of pollutant vapors. Recently, however, aerocolloids have been found to be formed when solid materials containing volatile components are exposed to sunlight. The purpose of this investigation was to determine the rate of formation of aerocolloids from various materials such as tar, roofing materials, and vinyl plastics upon irradiation. Once this base rate of aerosol formation was determined, various gases, e.g., sulfur dioxide, were added to the system to study their effect on the rate.

It was found in this research that the addition of 1.0 ppm SO_2 and 1.0 ppm NO_2 increases the mass of aerosols formed with those materials tested under sunlight irradiation with the exception of vinyl plastic. In the test with vinyl plastic, the rate of aerosol formation was approximately the same with air and 1.0 ppm SO_2 and a decrease was found when 1.0 ppm NO_2 was added to the system. When the test materials were irradiated with I. R. light, the results were too varied to make a correlation.

CHAPTER I

INTRODUCTION

Photochemical reactions in the atmosphere producing aerosols are extremely complex and have proven to be difficult to resolve. A vast number of reactants, many in very small quantities, are present in the air, and they are subjected to a great variety of conditions. Studies of aerosol formation are generally conducted with a limited number of reactants in a controlled environment for these reasons.

The factors which appear to be most significant in the production of aerosols from gaseous reactants are the concentrations of nitrogen oxides, sulfur dioxide, hydrocarbons, and ozone, and the sunlight intensity (1). That nitrogen oxides play a central role is well documented (1,2,3,4,5,6). Oxides of nitrogen, in excess of background levels, are introduced in urban air mainly by combustion processes and are emitted primarily as nitric oxide, NO. The rate of oxidation of NO to nitrogen dioxide, NO_2, in the atmosphere has been described by the equation (3,6)

$$\frac{d(NO_2)}{dt} = K_3(O_2)(NO)^2 - \frac{2K_1K_{a\emptyset}(NO_2)^2}{K_2(O_2)(M)}$$

where K_1 is the rate constant for atomic oxygen and NO_2, $K_{a\emptyset}$ the primary dissociation constant for NO_2, K_2 the atomic oxygen-molecular oxygen and

third body (M) rate constant, and K_3 the thermal rate of oxidation for nitric oxide. During periods of no sunlight, $K_a\emptyset$ is zero, and only the first righthand term of the equation is important. Beginning at sunrise, the second righthand term in the equation contributes. Although the presence of hydrocarbons alters the rate relationship, the equation shows that sunlight reduces the rate of formation of NO_2. The NO_2 also decomposes into atomic oxygen, O, and NO. The O is reactive and combines with molecular oxygen, O_2, to form ozone, O_3, or reacts directly with the hydrocarbons. It has been suggested that the atomic oxygen-hydrocarbon reaction is one of the chain-initiating steps in the formation of aerosols (6).

Sulfur exists in the atmosphere as hydrogen sulfide, H_2S, sulfuric acid, H_2SO_4, sulfur dioxide, SO_2, and as sulfate salts. Approximately 80% of the SO_2 in the atmosphere is emitted from the combustion of fossil fuels as H_2S which is rapidly converted to SO_2 (1,7). When SO_2 and O_3 are irradiated by sunlight, a very slow reaction occurs forming SO_3. The SO_3 then combines with atmospheric water vapor to form an aerosol of H_2SO_4. The rate of aerosol formation represents a conversion of SO_2 of approximately 0.07% per hour when the SO_2 concentration is 0.10 ppm and the O_3 concentration is 0.09 ppm. Increasing the O_3 concentration to 0.28 ppm results in a slightly higher rate of aerosol formation. When a hydrocarbon such as cis-pent-2-ene is added to the O_3-SO_2 system, a rapid increase in H_2SO_4 aerosol production takes place (8,9).

The importance of hydrocarbons in the creation of aerosols is further evidenced by the reactions they undergo with various pollutants to form aerosols. A study of the reactivity of hydrocarbons with O shows that hydrocarbons of four

or less carbon atoms and the respective OXO compounds (alcohols, acetone, methyl ethyl ketone) are unreactive, while hydrocarbons such as turpentine, isopropyl-benzene, cyclohexene, and cyclohexane are very reactive and form appreciable quantities of aerosols (10). In general, the most reactive hydrocarbons are those with double carbon bonds or carbon rings.

In addition to the gaseous hydrocarbons, polymers such as tars, plastics, paraffin wax, oil, and rubber have been studied to elucidate their contribution to aerosol formation in the atmosphere. A condensation aerosol is formed when polymers are heated (11). The temperature at which a specified number of nuclei are present on which aerosol particles can grow is referred to as the onset temperature. Successive heating of certain polymers changes the onset temperature. In general, if the flow temperature is greater than the onset temperature, each successive heating will require a higher temperature to generate a specified number of nuclei (12). This phenomenon is explained as being due to the weaker links of the polymer being broken at the lower temperatures which depletes the more easily broken links, necessitating a greater temperature in order to maintain a constant nuclei count (13). Polymers such as waxes have a flow temperature less than the onset temperature and therefore do not need a greater amount of energy to yield a particular nuclei count.

Studies on the effects of UV light and sunlight on polymers such as polyethylene terephthalate (PET) and polypropylene (PP) have shown that properties such as tensile strength, intrinsic viscosities, gel formation, and acid equivalents can be altered (14, 15, 16, 17, 18, 19, 20). These studies indicate that impurities

contained in polymers from manufacturing processes such as carbonyl, hydroxyl, aldehyde, ketone, carboxylic acid, and ester functional groups, and chromophores, absorb UV energy in the range of 290-400 mμ which can result in primary, bond-breaking reactions (17,18). Branched polymers are much more susceptible to UV oxidation reactions than linear polymers because of the tertiary hydrogen at each branch point. An examination of the volatile components of photoreactions show that the major products are CO, H_2O, and CH_3COCH_3. Studies with constant UV irradiation have shown that about every 10^{o} C rise in temperature doubles the rate of degradation (18).

Studies on polydienes (rubber) show that rubber can be attacked by oxygen at room temperature. When heat and light are added, the reaction is accelerated (21). The analysis of monomers formed from the pyrolysis of diene polymers indicates that approximately 25 wt % is methyl pentadiene, 6 wt % is 2-3-dimethylbutadiene, 5 wt % synthetic isoprene and traces of 1-3-butadiene, natural crepe rubber, balata, and chloroprene (22). When polydienes are exposed to U.V. irradiation, a series of very complex reactions takes place to form hydroperoxides. These hydroperoxides can then decompose, catalyzed by certain metallic impurities, to oxy alkyl polymer radicals which are susceptible to further reactions either with alkyl, alkoxy, or peroxy radicals or with atmospheric components (21).

Photo-oxidation and thermal degradation examinations on polyvinyl chloride (PVC) show that in both cases, degradation and crosslinking take place, with hydrogen chloride being released (21,23,24). The yellow color that is present in PVC that has aged requires a minimum of seven conjugated double bonds, and in

order for this to occur, the carbon atoms in the chain must lose either a hydrogen or chlorine atom. As the degradation process progresses, the residual chain gains in conjugation energy, resulting in a decrease in the activation energy for the next dehydro-chlorination step. In addition to crosslinking reactions which form double bonds, oxygen can react with the polymer at the radical site created by the loss of a chlorine or hydrogen atom to form unstable peroxy radicals (21).

Aerosols also can be formed when polymers are exposed to sunlight at temperatures below the onset temperature (25,26). In this case, the sunlight intensity determines the amount formed. The purpose of this investigation was to expose various polymers -- roofing material, vinyl plastic, asphalt, biodegradable plastic, and rubber -- to irradiation and to determine the effects of small amounts of SO_2 and NO_2 on the systems.

CHAPTER II

APPARATUS

A schematic representation of the experimental apparatus is shown in Figure 1. It consists basically of a dry air system, an exposure chamber, and a detection device. Dry air (Matheson, zero grade) passed through a pressure regulator and a flow control valve to a phosphorous pentoxide drying bed to further free the air of water vapor. The drying bed was made by packing phosphorous pentoxide in a 2-foot length of 3/8-inch Imperial Eastman "Poly-Flo" tubing. After drying, the air was filtered with a type VSWP (0.025μm pore size) Millipore filter.

From the filter, the air flowed to a valving system where the air could be directed into the exposure chamber or could be used to displace air containing nitrogen dioxide or anhydrous sulfur dioxide (both supplied by the Matheson Co.) from a 5-gallon glass vessel before flowing into the exposure chamber. A Hamilton microliter syringe, type 701-N, was used to place the desired volume of nitrogen dioxide or sulfur dioxide in the 5-gallon vessel.

The exposure chamber was a 10x10x5 cm (inside dimensions) box machined from a single block of aluminum and covered on one 10x10 cm face with a Vicor-quartz window. The window was fastened to the metal box by bolts and a retaining frame using a Teflon gasket. A separate aluminum plate was used to cover the

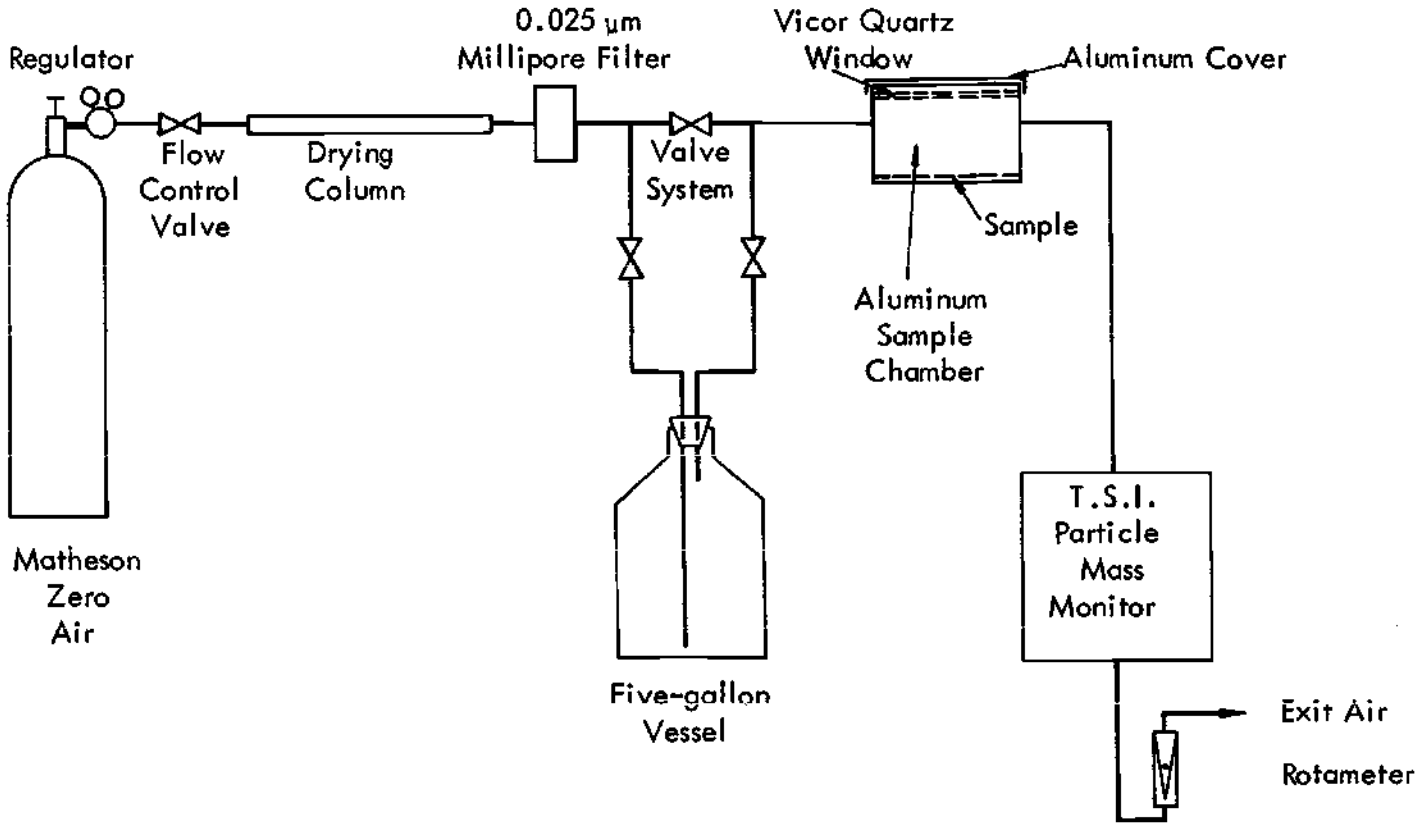

Figure 1. Apparatus

exposure chamber when sample irradiation was not desired. Inlet and outlet ports of 0.093 cm diameter were provided on opposite sides of the box.

The exiting air, vapor, and aerosol, or aerocolloid, stream passed directly to a Thermo-Systems Mass Monitor, Model 3205A, modified with a Matheson, No. 73, rotameter. The calibration curve for the rotameter appears in Appendix A. The sun intensity was measured on a day-to-day basis with a photometer distributed by the Weather Bureau Research Station at the Robert A. Taft Sanitary Engineering Center. It was calibrated against a system consisting of a Hewlett-Packard Radiant Flux Meter, Model 8330A, and a Radiant Flux Detector, Model 8334A, the calibration of which was traceable to the standards of the total irradiance of the National Bureau of Standards. The calibration curve for the photometer is shown in Appendix B. The output of the photometer was determined using a Leeds and Northrup millivolt potentiometer, Cat. No. 8686.

CHAPTER III

PROCEDURE

The apparatus was assembled on the roof of the four-story Chemical Engineering Building on the Georgia Tech Campus near downtown Atlanta. The tests were conducted in late May and June of 1973 and were done only on clear days to prevent clouds from shadowing the test material during the data collecting periods. Test material was cut to fill the bottom of the exposure chamber, placed in the chamber, the quartz window was replaced, and the aluminum cover was placed over the window.

Before tests were conducted, the system was flushed with dry air at a rate of 1.0 l/min for a minimum of 30 min. This flushing period also allowed sufficient time for the Particle Mass Monitor to warm to steady operating conditions. Once the Mass Monitor had warmed, 18.9 µl at room temperature and pressure of SO_2 or NO_2 was displaced into the 5-gallon glass vessel to create a 1.0 ppm mixture. The gas in the vessel was then mixed thoroughly by rolling the vessel which contained several loose pieces of "Poly-Flo" tubing. The sunlight intensity was measured and recorded.

At this time the Mass Monitor readout was checked to be assured of its constancy. With dry air flowing through the system and the Mass Monitor printer on, the aluminum cover was removed. Since only the steady-state particle production was desired, the aluminum reaction box was aligned with the

sun to allow maximum sunlight intensity on the sample.

Once a steady output of particles was observed, data collecting was begun. The time of the data collecting period was 600 sec.

Immediately after obtaining the particle production using dry air, the gas flow was directed through the 5-gallon glass vessel, displacing the air containing 1.0 ppm SO_2 or 1.0 ppm NO_2 through the exposure chamber. Again, data were taken after the system had reached a new steady production rate. The same collecting period was used as with the dry air.

Upon completion of the second part of the test period, the sunlight intensity was re-checked. In every instance, the sunlight intensity was the same before and after taking the data within the limits of experimental measurement. The tests were repeated at least once and normally twice.

Before the data were accepted as conclusive, it was deemed necessary to show that the production of particles was influenced by the sunlight and that the NO_2 or SO_2 was not reacting in some manner independent of the test material. To do this, two separate tests were made. On each material, tests were made as described above but the aluminum cover was left on the exposure chamber. This showed whether or not the NO_2 or SO_2 was reacting with the test material. The second test was designed to determine whether or not the NO_2 or SO_2 was reacting with the container or connecting tubing, causing particles to form. This test was made by passing dry air followed by air with 1.0 ppm SO_2 or NO_2 through the exposure chamber with the test material removed from the reaction box.

CHAPTER IV

PRESENTATION OF RESULTS

The test materials selected for this experimentation included plastic cup lids of biodegradable plastic, rubber gasket material, roofing material made with tar paper with small rocks over the tar paper, vinyl plastic car upholstery, and automobile lacquer paint. These materials were chosen because of their organic content. Other materials considered were wood, plant leaves, and fruit. These were not used because of their high water content which could react with SO_2 giving an acid mist detectable by the mass monitor. In order to eliminate moisture from the samples being tested, all samples were placed in a desiccator until they were used. Determining that the action of sunlight on the test materials produced particles, and showing that, in the absence of test materials, no particles were formed using air, 1.0 ppm SO_2, or 1.0 ppm NO_2, were the first objectives. To accomplish this, two preliminary tests were made.

The first test was to determine if particles could be produced in the absence of test material. Air was passed through the reaction box with the cover on and then with the cover off to determine if the cylinder air contained a component which could either produce particles or react with the aluminum box to produce particles. No detectable particles were produced in the presence or absence of sunlight. Cylinder air containing 1.0 ppm NO_2 was then passed through the reaction chamber to determine if the addition of the NO_2 would produce particles.

Again, no detectable particles were formed in the presence or absence of sunlight. Cylinder air containing 1.0 ppm SO_2 was then used. This test produced particles in both the presence and absence of sunlight. It was found that the cylinder air contained enough water vapor to produce acid particles and since air containing less water vapor was not available, the P_2O_5 drying tube, as described earlier, was added to the flow system. By trial and error, a tube length was found such that no detectable particles would be produced when cylinder air containing 1.0 ppm SO_2 was passed through the reaction chamber.

The second test was to determine if particles would be released by the test material in the absence of sunlight. To do this, each material was placed in the reaction chamber with the cover over the quartz window. Cylinder air was then passed over the test material. No detectable particles were formed with any of the test materials. Air containing 1.0 ppm NO_2 and air containing 1.0 ppm SO_2 were then passed over each test material in the absence of sunlight to determine if the addition of SO_2 or NO_2 to the air would cause particles to be produced. Again, no detectable particles were produced with any of the test materials.

Once it had been determined that particles were not formed in the absence of sunlight and that no particles were formed due to reactions with the aluminum reaction chamber, the next step was to investigate what effects the addition of sunlight would have.

Table 1* contains the data taken using roofing material as the test substance

* The data contained in Tables 1 through 15 represent actual readings from the Particle Mass Monitor printer.

Table 1. Aerosol Formation from Roofing Material Under Sunlight Irradiation with Air and 1.0 ppm SO_2

	Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
Air	100	1.1	0.006105	0.006105
	200	1.3	0.007215	0.01332
	300	0.9	0.004995	0.018315
	400	1.4	0.007770	0.026085
	500	1.6	0.008880	0.034965
	600	1.4	0.007770	0.042735
1.0 ppm SO_2	100	45.7	0.25364	0.25364
	200	47.2	0.26196	0.51560
	300	48.7	0.27029	0.78588
	400	46.1	0.25586	1.04174
	500	42.3	0.23477	1.27650
	600	44.2	0.24587	1.52237

to determine the effects of adding 1.0 ppm SO_2 to the system containing only the test substance, sunlight, and air. The data are also presented in Figure 2, which shows that the mass of particles produced in 600 sec was approximately 36 times greater when 1.0 ppm SO_2 was added. The rates of particle generation, the slopes of the curves, were 7.14×10^{-5} µg/sec for air and 2.54×10^{-3} µg/sec for 1.0 ppm SO_2. The sunlight intensity before and after the test was 0.58 watt/cm^2.

Table 2 shows the data taken to determine the effects of adding 1.0 ppm NO_2 to the system with roofing material as the test substance in the presence of sunlight. The data are graphically presented in Figure 3. The mass of particles collected using 1.0 ppm NO_2 was 4.2 times the mass collected when only air was present. The particle production rates were 6.34×10^{-5} µg/sec using air and 2.66×10^{-4} µg/sec using 1.0 ppm NO_2. The sunlight intensity remained constant during the test at 0.57 watt/cm^2.

The data collected with rubber as the test material to determine the effect of adding 1.0 ppm SO_2 to the system are presented in Table 3, and the information is also shown by Figure 4. The mass of particles produced in 600 sec increased from 0.10 µg when only air was passed through the system to 0.96 µg when 1.0 ppm SO_2 was added. The rates of particle production were 1.87×10^{-4} µg/sec for air and 1.60×10^{-3} µg/sec with 1.0 ppm SO_2, or an 850% increase. The sunlight intensity remained constant during these tests at 0.63 watt/cm^2.

When 1.0 ppm NO_2 was added to the system with rubber as the test material, the mass of particles produced increased in 600 sec from 0.12 µg for air to 0.18 µg using 1.0 ppm NO_2. Table 4 presents these data. The rates of particle formation,

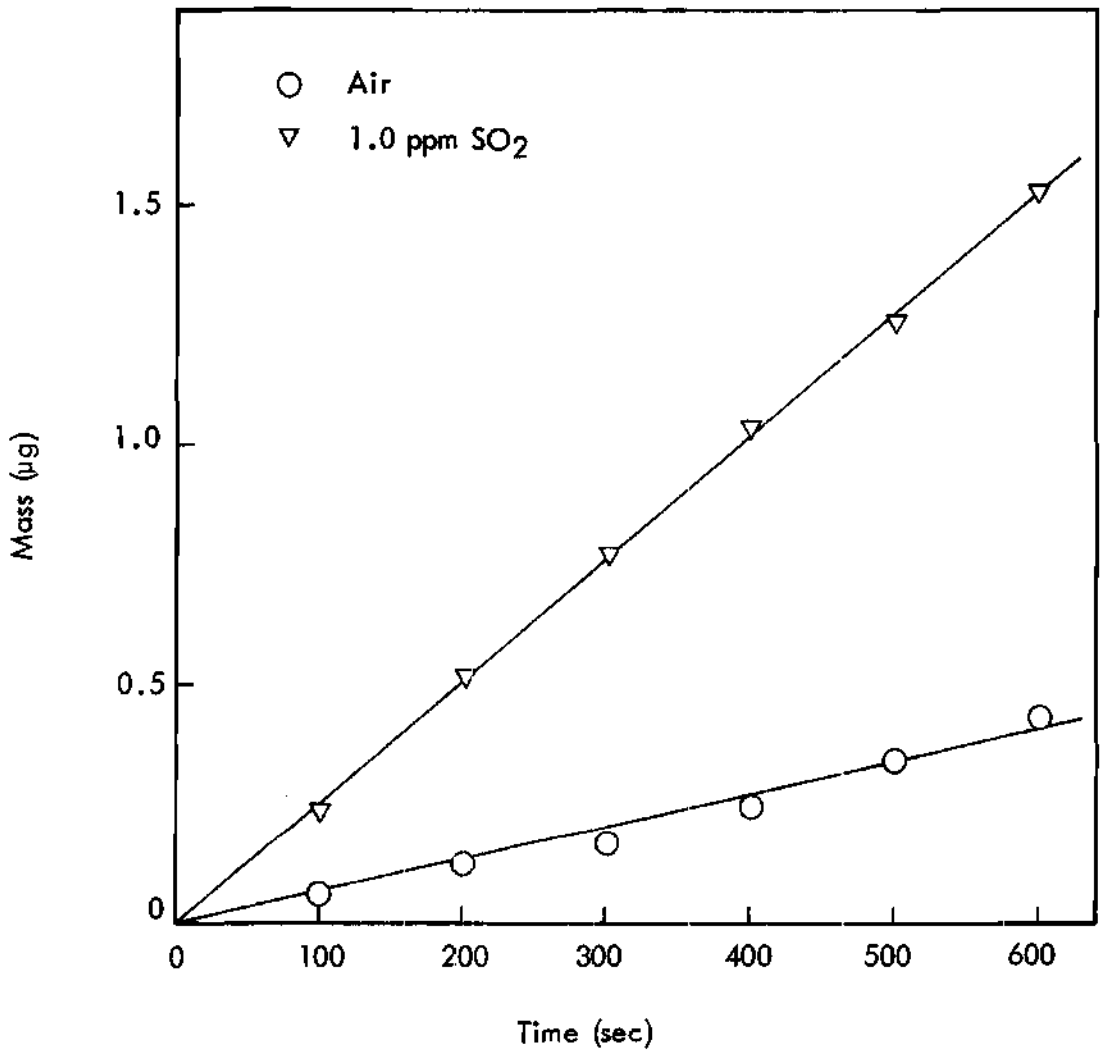

Figure 2. Aerosol Formation from Roofing Material Under Sunlight Irradiation with Air and 1.0 ppm SO_2.

Table 2. Aerosol Formation from Roofing Material Under Sunlight Irradiation with Air and 1.0 ppm NO_2

	Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
Air	100	1.0	0.00555	0.00555
	200	0.8	0.00444	0.00999
	300	1.3	0.007215	0.017205
	400	1.4	0.007770	0.024975
	500	1.3	0.007215	0.032190
	600	1.1	0.006105	0.038295
1.0 ppm NO_2	100	6.3	0.034965	0.034965
	200	3.9	0.021645	0.05661
	300	4.5	0.024975	0.081585
	400	5.2	0.028860	0.110445
	500	4.8	0.02664	0.137085
	600	4.1	0.022755	0.15984

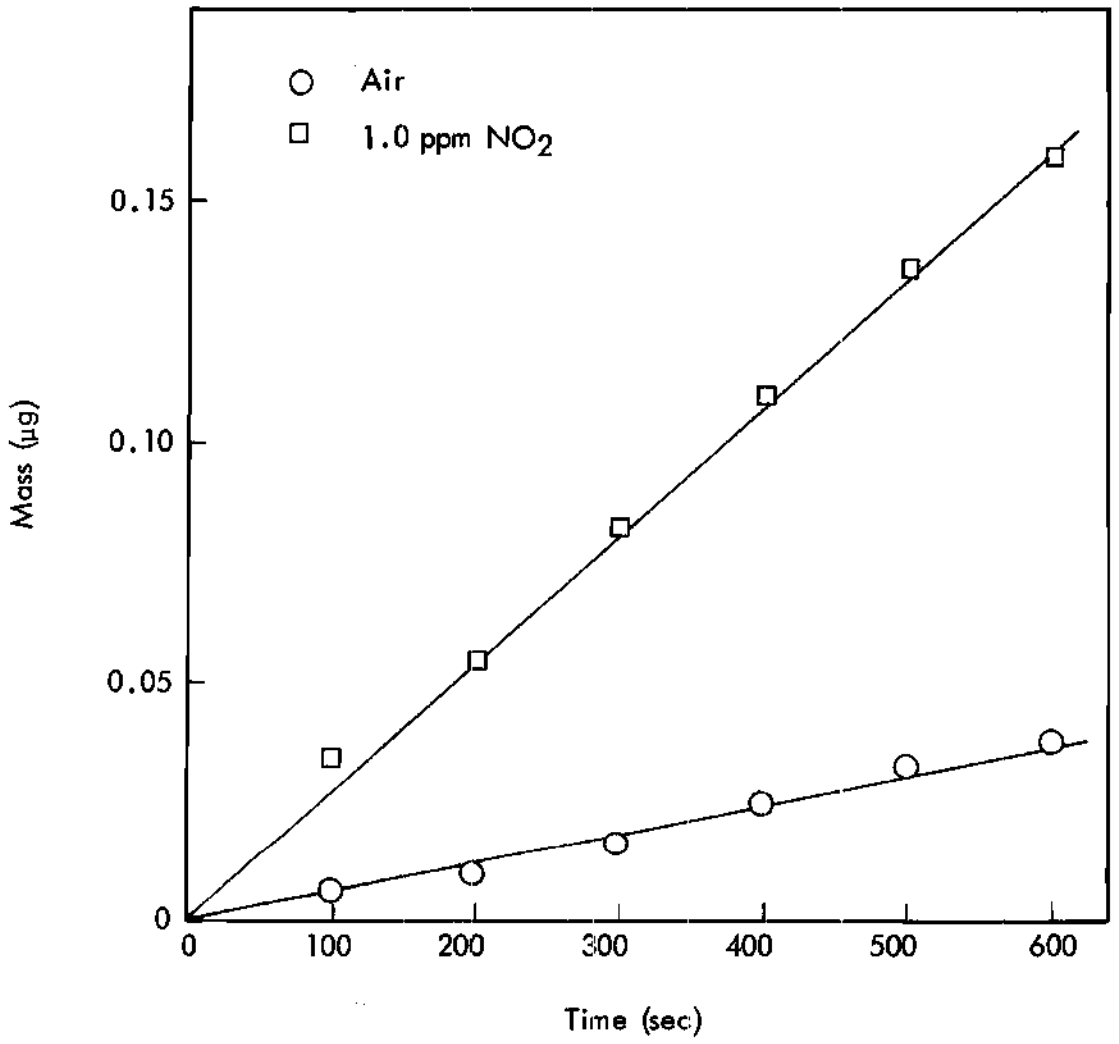

Figure 3. Aerosol Formation from Roofing Material Under Sunlight Irradiation with Air and 1.0 ppm NO_2.

Table 3. Aerosol Formation from Rubber Under Sunlight Irradiation with Air and 1.0 ppm SO_2

	Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
Air	100	3.0	0.01665	0.01665
	200	3.1	0.017205	0.033855
	300	2.6	0.01443	0.048285
	400	2.9	0.016095	0.06438
	500	2.7	0.014985	0.079365
	600	3.8	0.02109	0.100455
1.0 ppm SO_2	100	29.9	0.165945	0.165945
	200	27.9	0.154845	0.32079
	300	29.4	0.16317	0.48396
	400	30.8	0.17094	0.6549
	500	27.9	0.154845	0.809745
	600	26.6	0.14763	0.957375

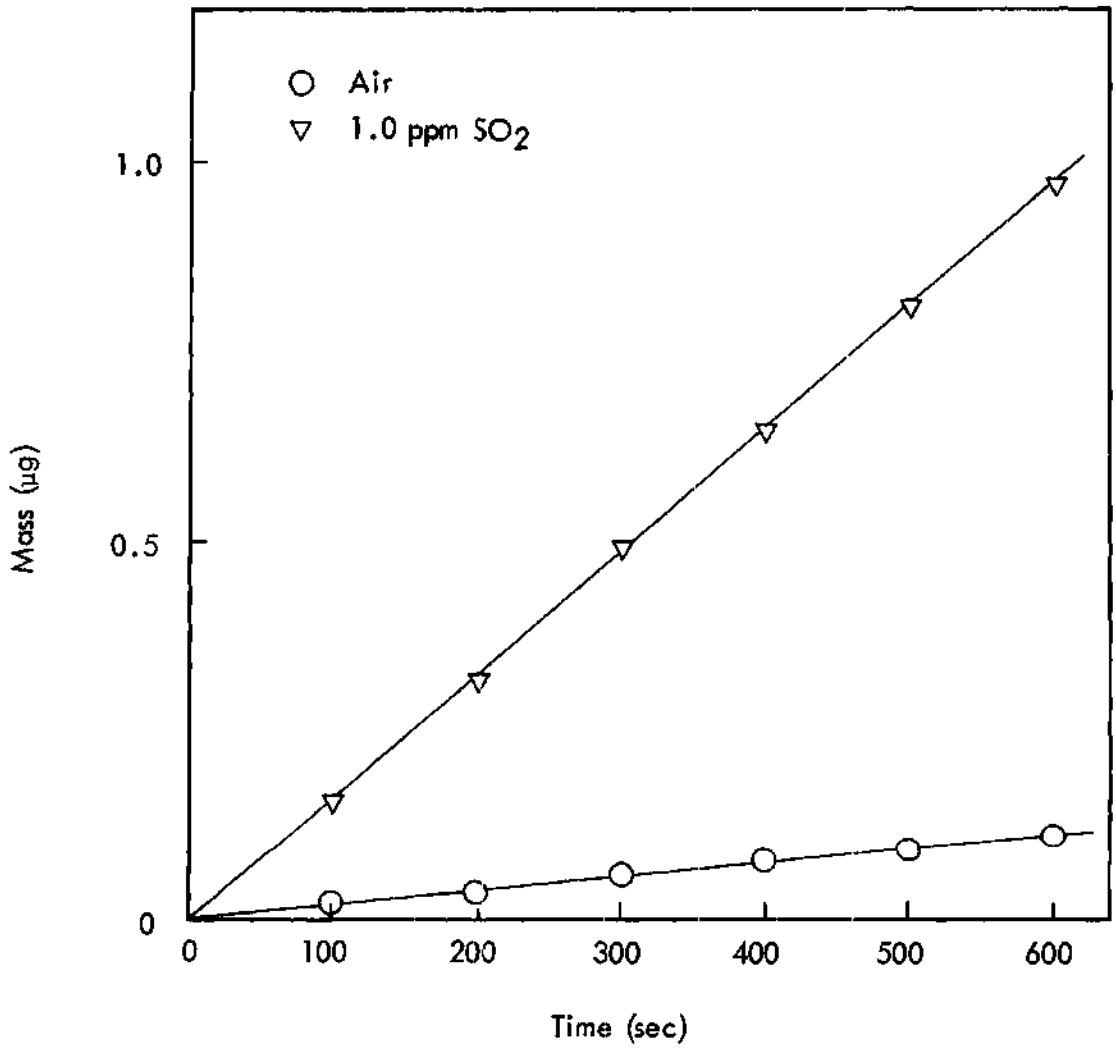

Figure 4. Aerosol Formation from Rubber Under Sunlight Irradiation with Air and 1.0 ppm SO_2.

Table 4. Aerosol Formation from Rubber Under Sunlight Irradiation with Air and 1.0 ppm NO_2

	Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
Air	100	2.6	0.01443	0.01443
	200	2.4	0.01332	0.02775
	300	4.4	0.02442	0.05217
	400	4.3	0.023865	0.076035
	500	2.8	0.01554	0.091575
	600	4.6	0.02553	0.117105
1.0 ppm NO_2	100	6.5	0.036075	0.036075
	200	4.4	0.02442	0.060495
	300	5.7	0.031636	0.09213
	400	3.9	0.021645	0.113775
	500	7.2	0.03996	0.153735
	600	4.9	0.027195	0.18093

determined from Figure 5, are 1.95×10^{-4} µg/sec for air and 3.02×10^{-4} µg/sec for 1.0 ppm NO_2. This rate increase amounted to 55%. Again, the sunlight intensity remained constant during the test and was 0.59 watt/cm^2.

The results obtained when vinyl plastic was examined were significantly different than those already tested. The data taken when the SO_2 effects were determined are presented in Table 5 and graphically shown in Figure 6. The mass of particles produced in 600 sec was 0.043 µg for air and very slightly more or 0.047 µg when 1.0 ppm SO_2 was introduced. This was only a 9% increase, the rates being 7.13×10^{-5} µg/sec for air and 7.77×10^{-5} µg/sec for 1.0 ppm SO_2. The sunlight intensity was 0.59 watt/cm^2 before and after the test.

When 1.0 ppm NO_2 was added to the system, a decrease in particle mass from 0.056 µg using air to 0.041 µg using 1.0 ppm NO_2 was observed. These data, presented in Table 6, show a 27% reduction in the mass of particles collected. The rates of particle production, calculated from Figure 7, were 9.9×10^{-5} µg/sec for air and 6.81×10^{-5} µg/sec for 1.0 ppm NO_2. During the experiment, the sunlight intensity remained at 0.60 watt/cm^2.

When biodegradable plastic and automobile lacquer paint were exposed to sunlight, no particle mass was detected during a test. When 1.0 ppm SO_2 was added to the system, no particles were detected. Likewise, no particles were produced when 1.0 ppm NO_2 was added to the system.

Asphalt produced particles when exposed to sunlight, and a change in the rate of particle output was noted when 1.0 ppm SO_2 was added to the system. When attempts were made to check the data, the mass monitor became irratic and

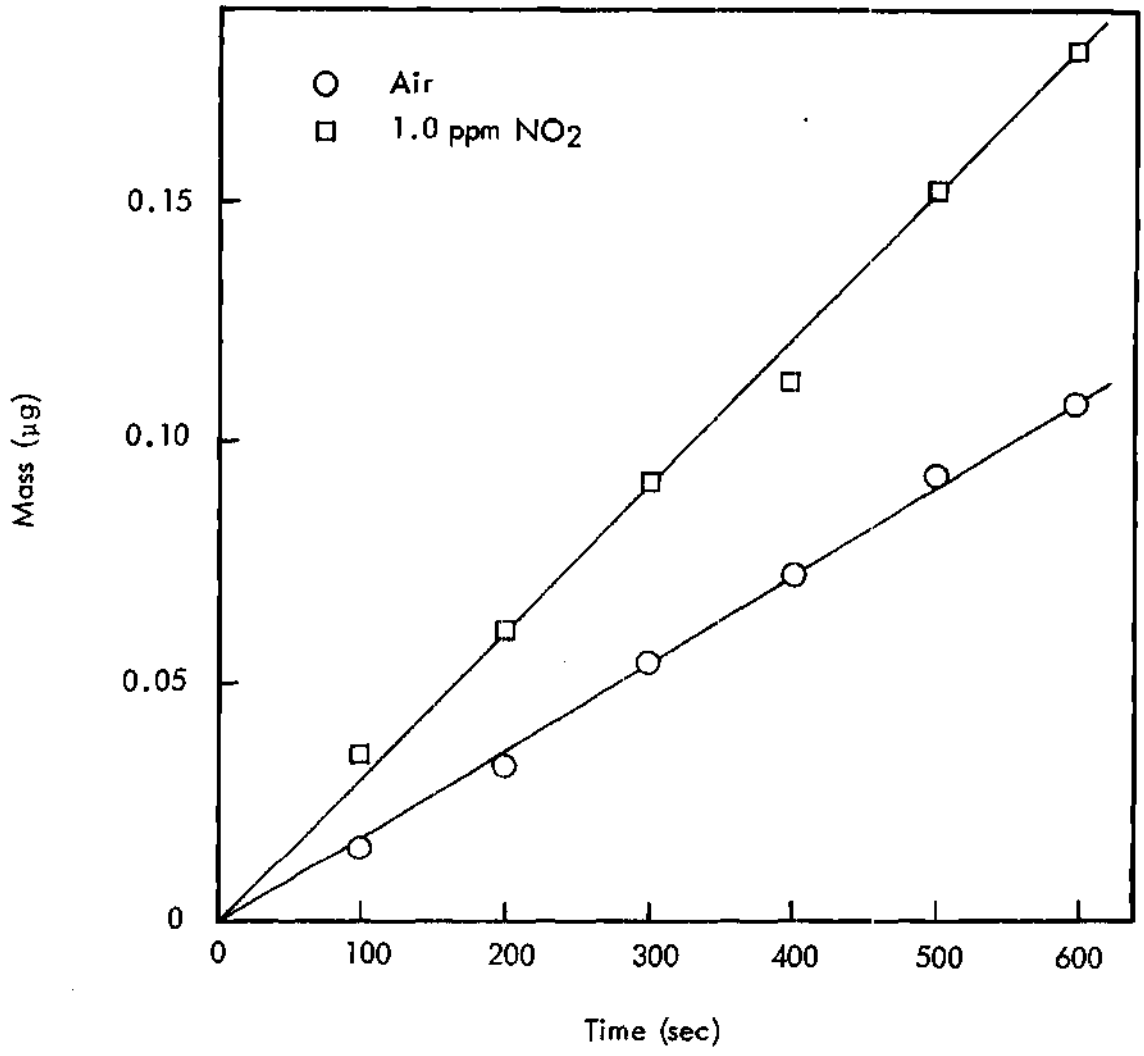

Figure 5. Aerosol Formation from Rubber Under Sunlight Irradiation with Air and 1.0 ppm NO_2.

Table 5. Aerosol Formation from Vinyl Plastic Under Sunlight Irradiation with Air and 1.0 ppm SO_2

	Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
Air	100	0.8	.00444	0.00444
	200	1.7	.009435	0.013875
	300	1.5	.008325	0.02220
	400	1.3	.007215	0.029415
	500	1.3	.007215	0.03663
	600	1.1	.006105	0.042735
1.0 ppm SO_2	100	1.4	.00777	0.00777
	200	1.6	.00888	0.01665
	300	1.2	.00666	0.02331
	400	1.3	.007215	0.030525
	500	1.6	.00888	0.039405
	600	1.3	.007215	0.04662

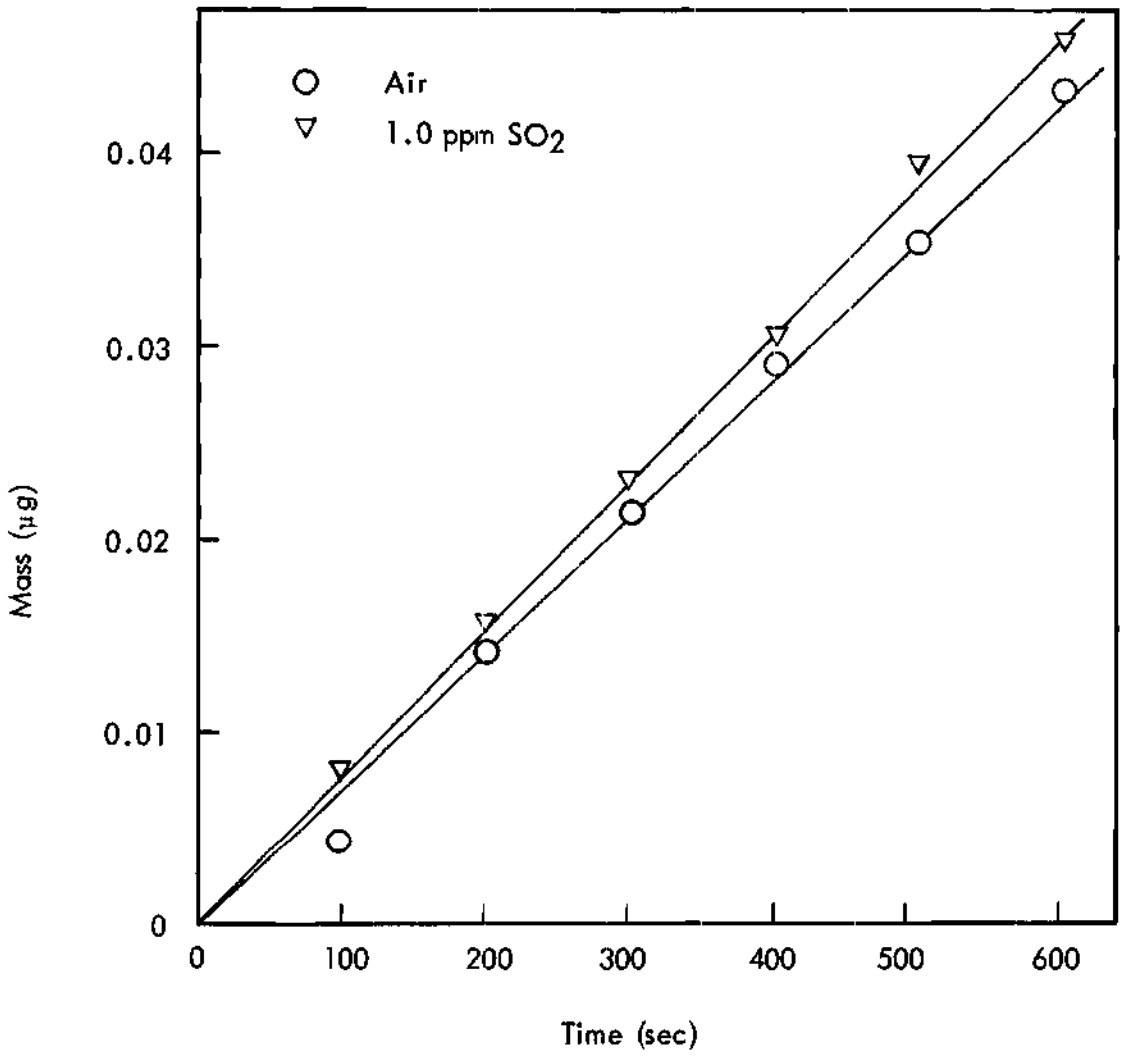

Figure 6. Aerosol Formation from Vinyl Plastic Under Sunlight Irradiation with Air and 1.0 ppm SO_2.

Table 6. Aerosol Formation from Vinyl Plastic Under Sunlight Irradiation with Air and 1.0 ppm NO_2

	Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
Air	100	1.2	0.00666	0.00888
	200	1.7	0.009435	0.016095
	300	2.4	0.01332	0.029415
	400	1.4	0.00777	0.037185
	500	1.6	0.00888	0.046065
	600	1.8	0.00999	0.056055
1.0 ppm NO_2	100	1.6	0.00888	0.00666
	200	1.1	0.006105	0.014985
	300	0.5	0.002775	0.01776
	400	1.0	0.00555	0.02331
	500	1.7	0.009435	0.032745
	600	1.5	0.008325	0.04107

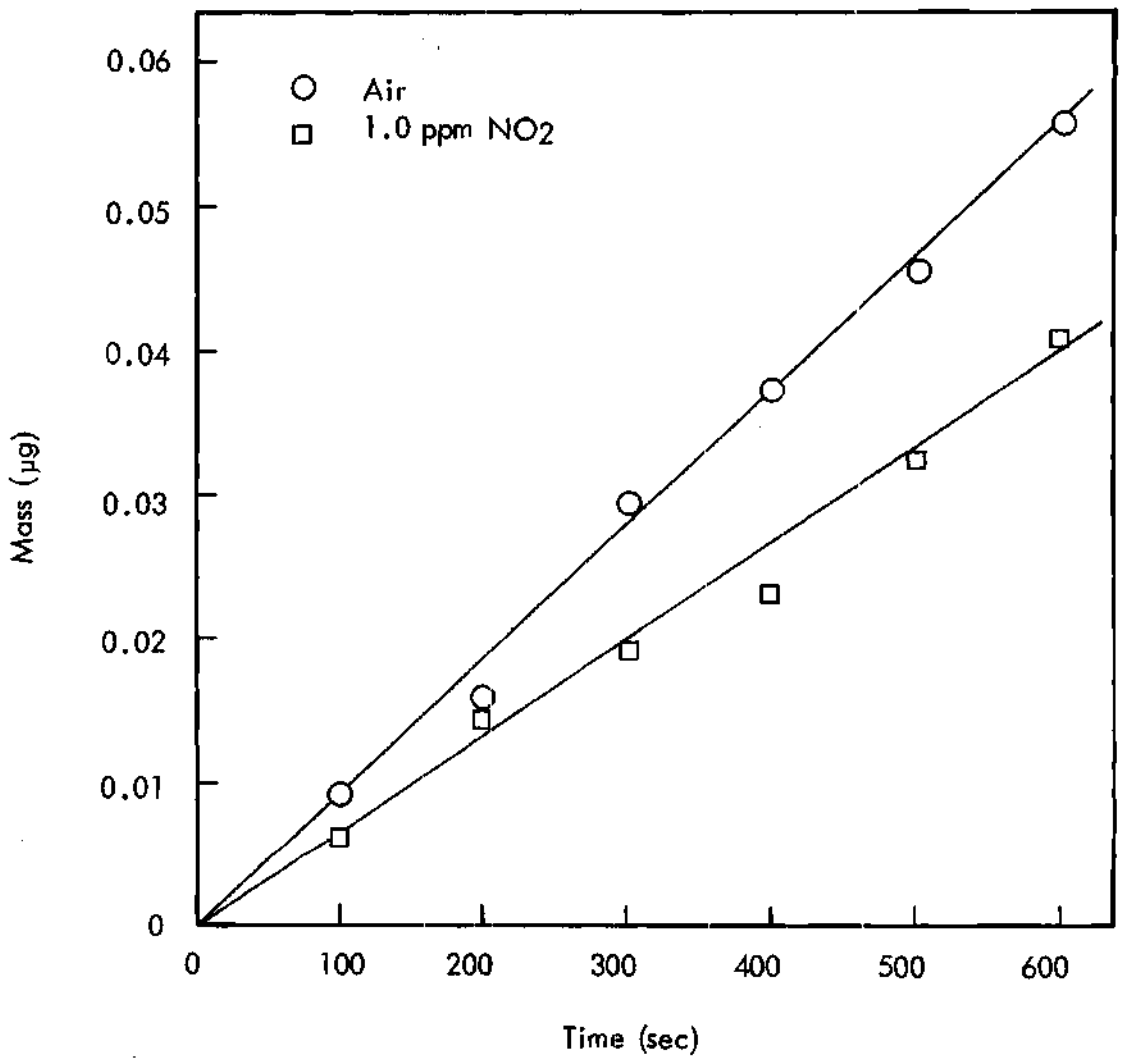

Figure 7. Aerosol Formation from Vinyl Plastic Under Sunlight Irradiation with Air and 1.0 ppm NO_2.

further useful data could not be obtained. The same results occurred again with a new set of crystals installed in the mass monitor. It appeared that the particles produced under these circumstances could not be cleaned entirely from the crystals, so further experimentation with asphalt was not made.

Additional tests were made on vinyl plastic, rubber, and roofing material in an attempt to establish more precisely the factors affecting the rate of particle generation. These tests were made in the laboratory using a General Electric infrared lamp as the light source. The intensity of the irradiation on each sample was 0.98 watt/cm^2; this value was checked daily.

The data for these additional tests were taken differently from the data collected using sunlight as the light source. Instead of finding the rate of particle production in air followed by the immediate addition of 1.0 ppm SO_2 or 1.0 ppm NO_2 to the system, each test was made separately with a clean system for each test.

The data collected using roofing material are presented in Tables 7, 8, and 9, and are shown collectively in Figure 8. The rate of aerosol formation using air was 9.44×10^{-5} µg/sec. When 1.0 ppm SO_2 was added, the rate decreased to 5.18×10^{-5} µg/sec. An increase was shown when 1.0 ppm NO_2 was used. The rate for 1.0 ppm NO_2 was 10.45×10^{-5} µg/sec.

The results obtained when vinyl plastic was examined using air are presented in Table 10. Tables 11 and 12 present the data collected when 1.0 ppm SO_2 and 1.0 ppm NO_2 were used in the system. The information contained in Tables 10, 11, and 12 are presented together in Figure 9. From Figure 9, the rate of particle generation was 10.9×10^{-4} µg/sec for air, 23.8×10^{-4} µg/sec for 1.0 ppm SO_2,

Table 7. Aerosol Formation from Roofing Material Under I. R. Irradiation with Air

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	1.0	0.00555	0.00555
200	2.4	0.01332	0.01887
300	1.1	0.006105	0.024975
400	2.1	0.011655	0.03663
500	2.4	0.01332	0.04995
600	1.2	0.00666	0.05661

Table 8. Aerosol Formation from Roofing Material Under I. R. Irradiation with 1.0 ppm SO_2

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	1.0	0.00555	0.00555
200	1.2	0.00666	0.01221
300	1.2	0.00666	0.01887
400	0.4	0.00222	0.02109
500	0.8	0.00444	0.02553
600	1.0	0.00555	0.03108

Table 9. Aerosol Formation from Roofing Material Under I. R. Irradiation with 1.0 ppm NO_2

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	1.7	0.009435	0.009435
200	1.6	0.00888	0.018315
300	1.5	0.008325	0.02664
400	2.1	0.011655	0.038295
500	2.2	0.01221	0.050505
600	2.2	0.01221	0.062715

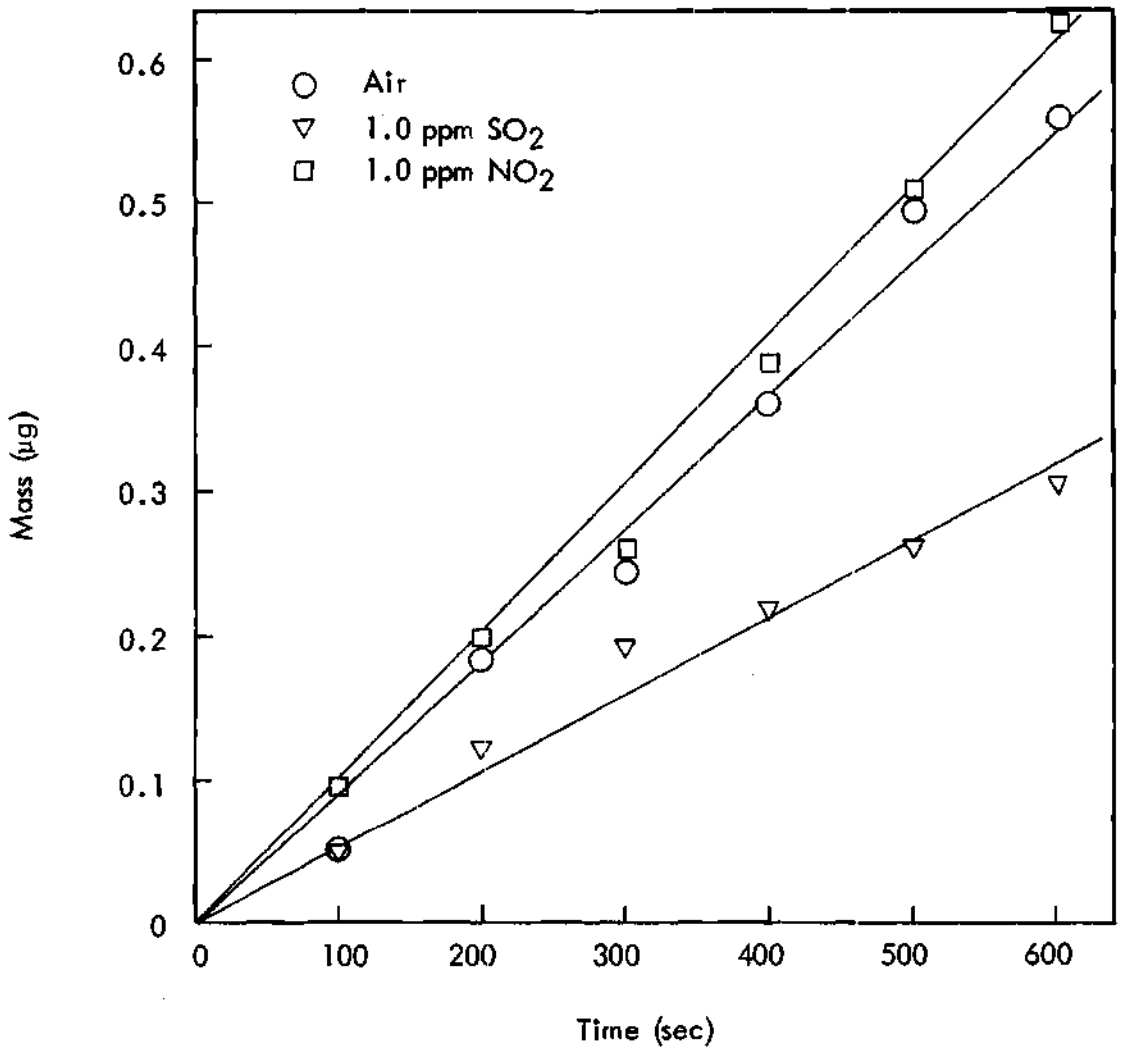

Figure 8. Aerosol Formation from Roofing Material Under I. R. Irradiation with Air, 1.0 ppm SO_2, and 1.0 ppm NO_2.

Table 10. Aerosol Formation from Vinyl Plastic Under I. R. Irradiation with Air

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	15.0	0.08325	0.08325
200	22.4	0.12432	0.20757
300	20.4	0.11322	0.32079
400	18.6	0.10323	0.42402
500	24.3	0.134865	0.558885
600	17.1	0.094905	0.65379

Table 11. Aerosol Formation from Vinyl Plastic Under I. R. Irradiation with 1.0 ppm SO_2

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	34.2	0.18981	0.18981
200	50.9	0.282495	0.472305
300	39.9	0.221445	0.69375
400	40.3	0.223665	0.917415
500	53.3	0.295815	1.21323
600	38.9	0.215895	1.429125

Table 12. Aerosol Formation from Vinyl Plastic Under I. R. Irradiation with 1.0 ppm NO_2

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	4.9	0.027195	0.027195
200	7.3	0.040515	0.06771
300	6.9	0.038295	0.106005
400	4.9	0.027195	0.1332
500	9.4	0.05217	0.18537
600	6.9	0.038295	0.223665

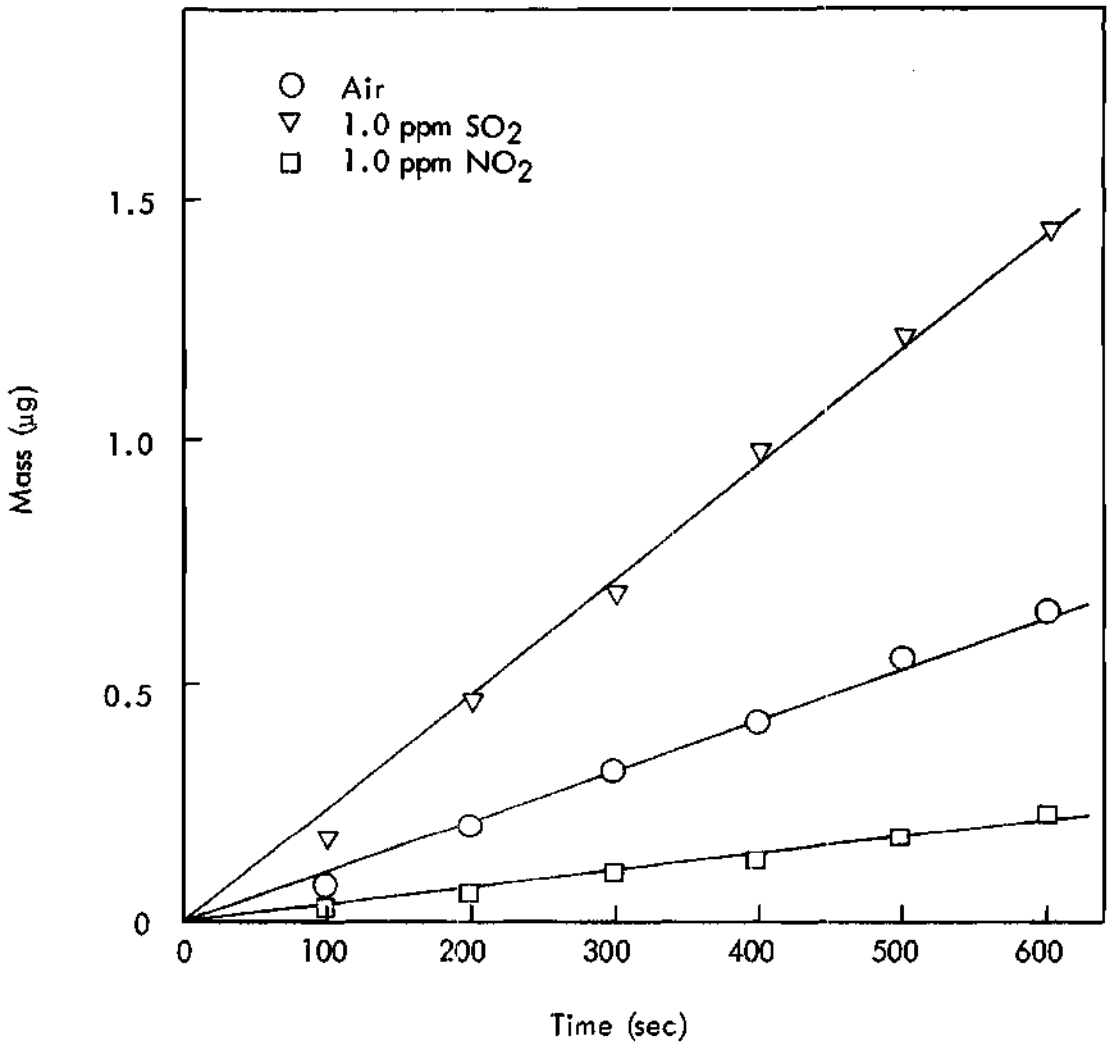

Figure 9. Aerosol Formation from Vinyl Plastic Under I. R. Irradiation with Air, 1.0 ppm SO_2, and 1.0 ppm NO_2.

and 3.73×10^{-4} µg/sec for 1.0 ppm NO_2.

Tables 13, 14, and 15 show the data obtained when rubber was used as the test material with air, 1.0 ppm SO_2, and 1.0 ppm NO_2. These data are shown again together in Figure 10. From Figure 10 the rates were determined to be 5.22×10^{-4} µg/sec for air, 7.83×10^{-4} µg/sec for 1.0 ppm SO_2, and 5.91×10^{-4} µg/sec for 1.0 ppm NO_2.

Table 13. Aerosol Formation from Rubber Under I. R. Irradiation with Air

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	5.0	0.02775	0.02775
200	6.5	0.036075	0.063825
300	10.8	0.05994	0.123765
400	10.5	0.058275	0.18204
500	8.6	0.04773	0.22977
600	9.4	0.05217	0.28194

Table 14. Aerosol Formation from Rubber Under I. R. Irradiation with 1.0 ppm SO_2

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	9.0	0.04995	0.04995
200	11.1	0.061605	0.111555
300	16.5	0.091575	0.20313
400	13.9	0.077145	0.280275
500	13.8	0.07659	0.356865
600	14.1	0.078255	0.43512

Table 15. Aerosol Formation from Rubber Under I. R. Irradiation with 1.0 ppm NO_2

Time (sec)	ΔF	Mass (μg)	Mass Accumulation (μg)
100	7.7	0.03330	0.03330
200	6.0	0.046065	0.079365
300	11.4	0.063270	0.142635
400	11.9	0.066045	0.20868
500	10.0	0.05550	0.26418
600	10.6	0.05883	0.32301

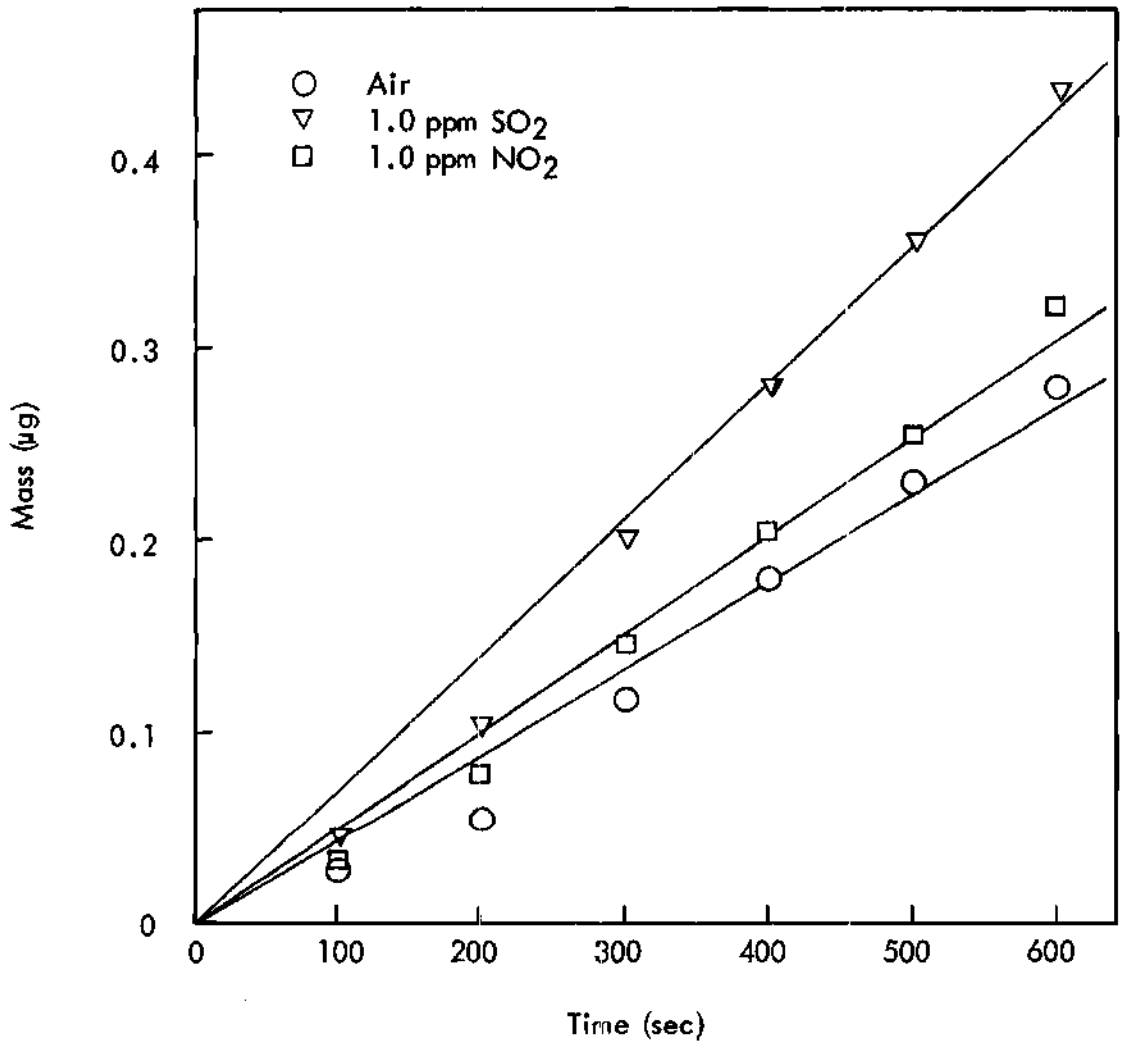

Figure 10. Aerosol Formation from Rubber Under I. R. Irradiation with Air, 1.0 ppm SO_2, and 1.0 ppm NO_2.

CHAPTER V

DISCUSSION OF RESULTS

When this research was begun, it was anticipated that materials such as vinyl plastic, rubber, and roofing material would produce aerosol particles when exposed to irradiation and the addition of SO_2 or NO_2 would increase the mass of particles being produced. In the first part of this work using the sun for irradiation, a significant increase in the amount of aerosols was found when SO_2 or NO_2 was added to the system containing rubber and roofing material. The results obtained using vinyl plastic did not correlate with rubber or roofing material. Table 16 summarizes these results.

When 1.0 ppm NO_2 was added to the system using vinyl plastic, a decrease in particle production was found, and when 1.0 ppm SO_2 was added, a very slight increase in particle production was shown. There are at least three possibilities that may explain these results. The first is derived from the finding of Walther, et al., (13) that CO inhibits particle production by pyrolysis. This was explained as deriving from the carbonyl form tying up bonds that would normally break to form particles. It may be that when SO_2 was added to the system, the SO_2 reacted to tie up the bonds that normally broke to form particles. If this is what transpires, it indicates that the structure of the vinyl plastic molecules is significantly different from the structures of roofing material and rubber.

Table 16. Summary of Aerosol Formation Rates

		IR Irradiation I = 0.98 watts/cm^2		Sunlight Irradiation	
		Rate (µg/sec)		Rate (µg/sec)	I (watts/cm^2)
Vinyl Plastic	Air	109×10^{-5}	Air	7.13×10^{-5}	0.59
	SO_2	238×10^{-5}	SO_2	7.77×10^{-5}	
	NO_2	37.3×10^{-5}	Air	9.9×10^{-5}	0.60
			NO_2	6.81×10^{-5}	
Rubber	Air	52.2×10^{-5}	Air	18.7×10^{-5}	0.63
	SO_2	78.3×10^{-5}	SO_2	160×10^{-5}	
	NO_2	59.1×10^{-5}	Air	19.5×10^{-5}	0.59
			NO_2	30.2×10^{-5}	
Roofing Material	Air	9.44×10^{-5}	Air	7.14×10^{-5}	0.58
	SO_2	5.18×10^{-5}	SO_2	254×10^{-5}	
	NO_2	10.45×10^{-5}	Air	6.34×10^{-5}	0.57
			NO_2	26.6×10^{-5}	

The second possibility concerns the particles themselves. During experimentation, there were times when clouds would shade the experimental apparatus from the sun. When this happened, the mass monitor would indicate a reduction in particle mass. A similar reduction in mass also occurred when the aluminum cover was placed over the exposure chamber, suggesting that a portion of the aerosol particles are extremely volatile. Since particle production rates for vinyl plastic with 1.0 ppm SO_2 and 1.0 ppm NO_2 do not increase as did rubber and roofing material, it could be that a greater percentage of the particles formed with vinyl plastic are volatile than with rubber or roofing material. As experimentation progressed, evaporation of the particles from the sensor crystal, once they had been collected, would indicate a lower mass rate of production.

The third method to explain why aerosol particle production is reduced when 1.0 ppm NO_2 was added to the vinyl plastic system could be related to the observation that oxidation reactions compete with crosslinking during U.V. irradiation (25). If the NO_2 inhibits the oxidation reaction and allows the crosslinking reaction to dominate, a lower particle production rate would be observed.

Conversely, the addition of 1.0 ppm SO_2 could aid in the oxidation reaction giving an increase in the rate of aerosol production.

The similar results obtained using rubber and roofing material is probably due to the fact that their compositions are closely related in that they both are composed of unsaturated hydrocarbons. The rubber is a branched polydiene while the composition of asphalt includes saturated and unsaturated hydrocarbons, the unsaturated hydrocarbons being primarily napthenes and polynapthenes. The part-

icles generated from rubber and asphalt are apparently due to partially oxidized polymers produced during the U. V. irradiation with additional reactions taking place when NO_2 or SO_2 is introduced into the system.

The biodegradable plastic, a linear, unsaturated hydrocarbon, did not produce any detectable particles during the experimentation. This is probably due to the fact that polymers which are not branched are not as easily photo-oxidized. Also, if a very small amount were produced, detection would be difficult because of the instability of the particles.

Paint, a highly crosslinked polymer, would not be expected to produce particles on the premise that if crosslinking reactions occurring in vinyl chloride reduce aerosol generation, a polymer already composed of crosslinked polymers would likewise not produce particles. Also, in a highly crosslinked system, a larger number of chain scission reactions must occur before c low molecular weight (volatile) compound can be released. Thus, a high degree of crosslinking should lead to reduced aerosol generation, as observed.

In the second part of this research the same samples that had been exposed to sunlight were exposed to infrared light at an intensity of 0.98 watt/cm^2 or approximately 50% more energy than with sunlight. In this part of the experimentation, results were found similar to those described by Walther, et al. (12,13); namely, that the onset temperature increased with successive heatings. In this research it was found that the mass of particles produced decreased, at a constant light intensity, with successive tests. This phenomenon makes comparison of data in the second part of this research difficult. Nevertheless, some insight can be

gained as to how the particles are generated with sunlight.

Examination of the data from both parts of this research show that the order of magnitude of particle mass generation is the same. The data in the first part of this study, with sunlight, show that particles were produced at various rates with approximately 0.60 watt/cm^2 of energy. The second part of this study, using I. R. irradiation at 0.98 watt/cm^2, showed similar outputs of mass. This suggests that the production of particles is due both to the heating effect and to the ultraviolet rays from the sunlight.

Differences in particle generation in using the infrared lamp versus sunlight for the materials studied can best be explained by the selective absorption characteristics of organic materials. In particular, the absorption of I.R. and U.V. radiation by specific materials is not expected to be proportionally related.

CHAPTER VI

CONCLUSIONS

The conclusions resulting from this work are summarized as follows:

1. Sunlight irradiation on organic materials such as rubber, vinyl plastic, and roofing material results in aerosol particles.

2. Infrared irradiation on organic materials such as rubber, vinyl plastic, and roofing material leads to aerosol particles.

3. The presence of low concentrations of air pollutants such as NO_2 and SO_2 alters the mass of aerosols produced by irradiation of these same organic materials.

4. At least a portion of the particles produced by the irradiation of organic materials is unstable.

5. No particles were detected when biodegradable plastic or automobile lacquer paint was examined.

CHAPTER VII

RECOMMENDATIONS

It is recommended that this research be continued and that the following specific determinations be made:

1. The temperatures organic materials attain under irradiation test conditions should be measured. This will aid in establishing the reason for the difference between infrared light and sunlight on particle production.

2. The chemical and physical characteristics of the aerosol particles produced under irradiation should be examined. From their composition and physical properties, much could be learned of the mechanism by which the particles are formed.

3. Further testing of materials irradiated here only by ultraviolet light should be accomplished to see if particles are formed.

4. Examine various classes of polymers such as polydienes and halogenated polymers in order to determine if each class of polymer behaves similarly.

APPENDICES

APPENDIX A

ROTAMETER CALIBRATION CURVE

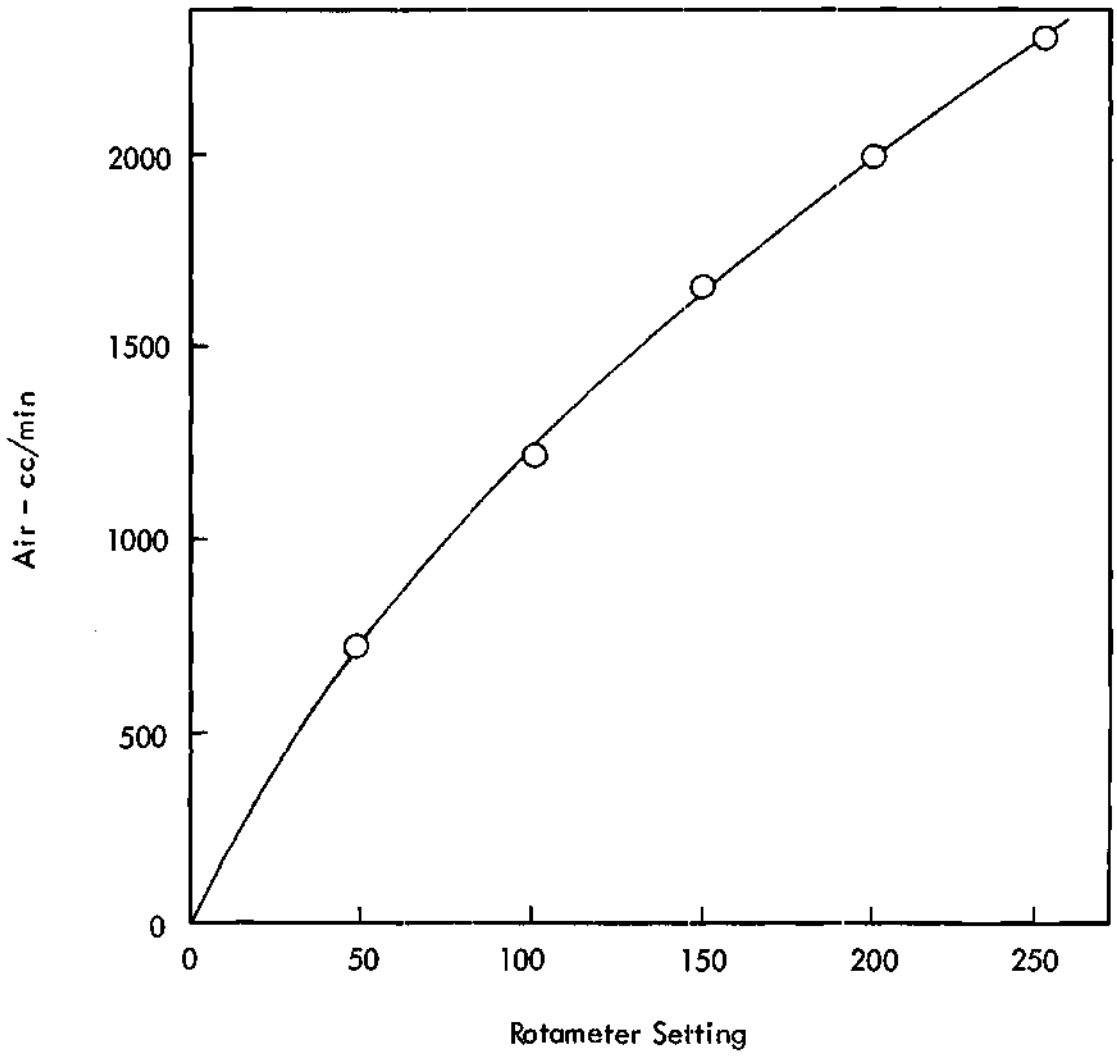

Figure 11. Filtered, Dry Air Rotameter Calibration Curve.

APPENDIX B

PHOTOMETER CALIBRATION CURVE

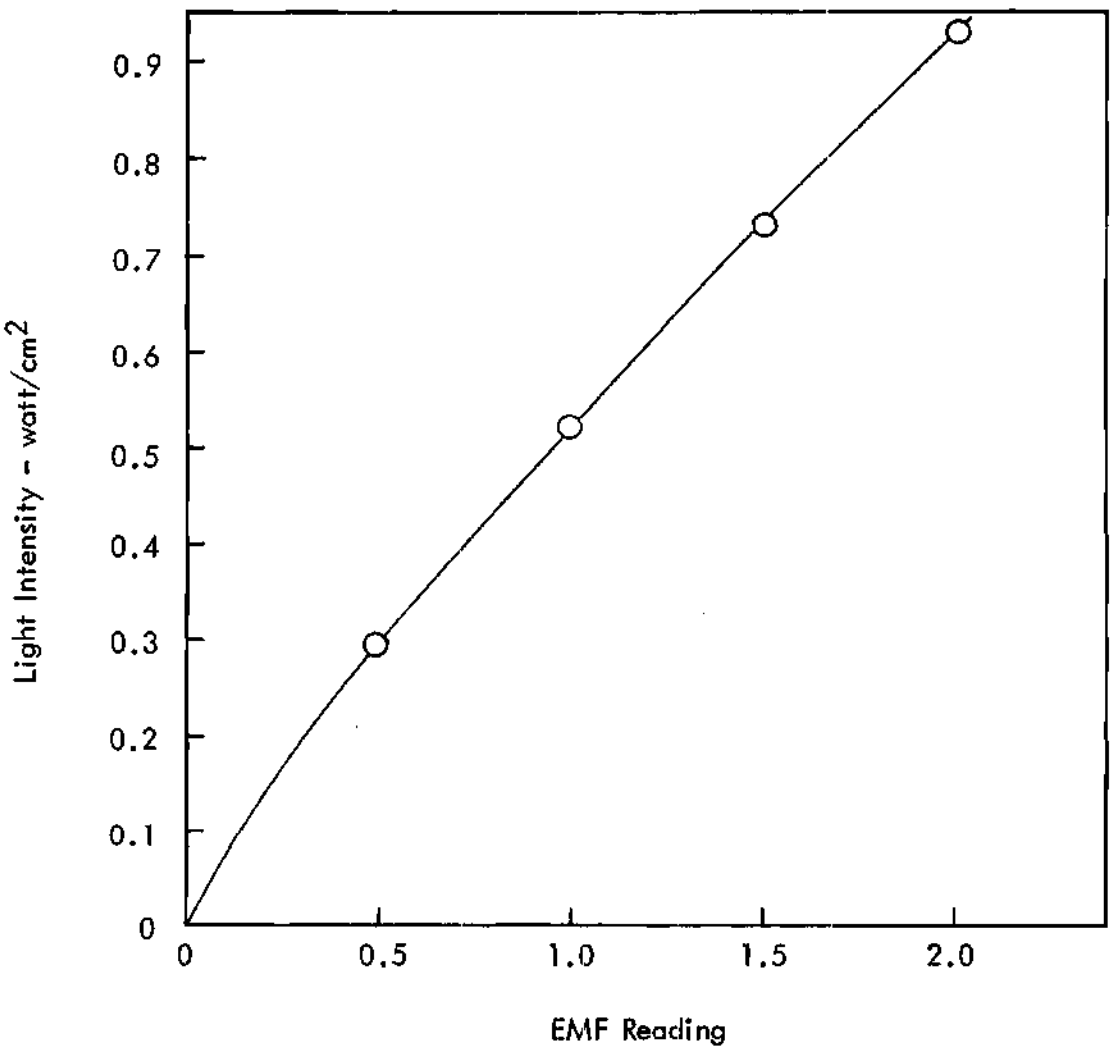

Figure 12. Energy Conversion Curve for Photometer.

APPENDIX C

PARTICLE MASS CALCULATIONS*

The Particle Mass Monitor instrument incorporates a quartz crystal oscillating at its resonance mechanical frequency of vibration. When particle mass is precipitated on the crystal, its resonance frequency decreases linearly. This change in vibrating frequency is directly proportioned to the total mass added to the crystal.

The mass sensitivity, S, of the crystal vibrating at its fundamental thickness-shear mode is

$$S = \frac{\Delta F}{\Delta M} = - \frac{2.27\ F_o^2}{A} \qquad (1)$$

The particle mass concentration, C, is then

$$C = \left(\frac{1}{SQE_cE_w}\right) \frac{\Delta F}{\Delta t} \qquad (2)$$

With E_c and E_w being 100%, A being 0.3167 cm^2, and Q being 1 liter per minute, S then becomes

$$S = 180\ Hz/\mu g \qquad (3)$$

* Reference (27).

and the particle mass concentration C becomes

$$C = 333 \frac{\Delta F}{\Delta t} \tag{4}$$

with the units of C being g/m^3.

To determine the mass M being deposited, Equation (4) is multiplied by the amount of gas flowing through the system in 60 seconds or 1 liter per min and M becomes

$$M = C \frac{1000 cm^3}{60 \text{ sec}} \cdot \frac{m^3}{10^6 cm^3} \tag{5}$$

$$M = \frac{C}{6 \times 10^4} \tag{6}$$

$$M = 0.00555 \, \Delta F \tag{7}$$

with M being in micrograms.

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